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(54) IMPROVEMENTS IN AND RELATING TO CONSTRUCTIONAL MATERIALS

(71) We, HOECHST AKTIENGESELL-SCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us. and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to constructional materials comprising an inorganic binding agent, and its additives therefor.

It is already known that plastics dispersions can be used as an additive for mortar and concrete. The addition of such plastics dispersions, for example, dispersions based on styrene and acrylonitrile is described in German Offenlegungsschrift No. 1,471,153. Furthermore it is known from German Offenlegungsschriften Nos. 1,671,017 and 1,909,681 that water-soluble polycondensates, for example, sulphite and sulphonic acid modified resins based on an amino - s - triazine having at least two NH2 groups in the form of aqueous solutions or water-free pulverized resins may be used as additives for mortar and concrete. The combined addition of polymers of olefinically unsaturated compounds 30 and polycondensates of modified amino - s triazines to the concrete or mortar mixtures is also described. In this process the polymer is incorporated into the mortar mixture in the form of a dispersible powder together with the solid or dissolved polycondensate and optionally further additives, according to German Auslegeschrift No. 2,102,456, or a mixture of an aqueous plastics dispersion and an aqueous polycondensate solution is spray dried and added to the mortar in the form of a dried powder according to German Auslegeschrift No. 2,049,114.

The use of polymers in the form of a spray dried dispersible powder has, however,

cess irreversibly modifies the properties of the polymer particles. A powder dispersible in water contains substantially coarser polymer particles than the starting dispersion wherefrom it has been prepared and has therefore a greater tendency towards sedimentation. The viscosity of the starting and final dispersion having the same polymer content each time are moreover variable. Owing to the fact that the sensitive emulsifier-protective colloid system is unfavourably affected by the drying process, the final dispersions prepared from the dispersible powders are altogether less stable than the starting dispersions obtained by emulsion polymerization.

The present invention is based on our surprising observation that the properties of a concrete or mortar containing an aminoplast polycondensate can be further improved by adding an aqueous dispersion of a polymer, which dispersion is obtained by emulsion polymerization. If the polymer dispersion is added in its original form, the polymer particles are generally incorporated into the concrete or mortar mixture in a finely divided form, thus affecting the strength properties far more favourably than a dispersion of the same composition in the form of a spray dried dispersible powder having essentially coarser particles. Furthermore, not all polymer dispersions can be spray dried in a satisfactory manner so that the choice and combination possibilities are substantially greater if aqueous plastics dispersions are used.

The sulphite modified polycondensates are modified by sulphite or bisulphite salts or sulphurous acid. Advantageously amino - s - triazines in which there are two or more amino groups, are used and especially melamine.

The present invention provides a composition comprising an inorganic binding agent, a sulphite modified polycondensate of formaldehyde and an amino - s - triazine, and a series of inconveniences. The drying pro- polymer of one or more olefinically unsatur-

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ated monomers, the said polymer having been incorporated in the form of an aqueous dispersion formed by emulsion polymerization.

There may be mentioned as suitable unsaturated monomers the vinvl esters of saturated monocarboxylic acids, for example, vinyl acetate, vinyl propionate, vinyl isobutyrate, vinyl laurate, and vinyl versatate (trade mark, see below); acrylic or methacrylic acid esters, for example ethyl acrylate or methyl methacrylate; vinyl or vinylidene halides, for example vinyl chloride and vinylidene chloride; unsaturated hydrocarbons, for example ethylene, styrene, vinyl toluene, and butadiene; and acrylonitrile. Especially preferred are dispersions which are saponifiable only with difficulty or not at all, e.g. those comprising a polymer relatively resistant to the action of alkalies are especially preferred. Examples of such plastics dispersions are copolymer dispersions of vinyl acetate/vinyl chloride, vinyl propionate/vinyl chloride, vinyl acetate/ ethylene, vinyl acetate/vinyl chloride/ethylene, vinyl acetate/ vinyl chloride/vinyl laurate, styrene/butyl acrylate, styrene/butadiene, styrene/acrylonitrile, butyl acrylate/methyl methacrylate, and butyl acrylate/vinylidene chloride, or a copolymer dispersion of vinyl acetate and vinyl esters of tertiary acids 30 having from 9 to 11 carbon atoms, such as versatic (911) acid (trade mark).

Many properties of known concrete or mortar mixtures containing a polycondensate of modified amino - s - triazines are generally improved by the addition of the aqueous polymer dispersion, such as the water retaining power of the freshly mixed mortar; the working properties (which improvement makes it possible to reduce the water/binding agent co-efficient), the cohesiveness of the mortar in working, for example in pumping, roughcasting, or finishing the adhesion of the freshly mixed or hardened mortar to the substrate; the elasticity and tensile strength in binding. Furthermore stresses which occur during age hardening are less and therefore the susceptibility to cracking is reduced. In addition, the waterproofness is increased.

If as in the previously proposed processes, the poly- is used in the form of a dried dispersible powder, this improvement is in general not obtained to the same degree.

The present invention also provides a process for the preparation of a composition as defined above, which comprises admixing the inorganic binding agent, the sulphite modified polycondensate of formaldehyde and amino s - triazine and the polymer, the polymer being incorporated in the form of an aqueous dispersion formed by an emulsion polymerization process.

The aqueous polymer dispersion can be added to the mortar mixture as such or together with the batch water. A mixture of the aqueous polymer dispersion and the aqueous polycondensate solution is, however, preferably used. In order to ensure the compatibility of the systems, the pH of mixture is preferably adjusted to a value greater than 7, advantageously greater than 8, and especially from 8 to 9, with alkaline agents. In this way the mixture remains stable and storable over a long period of time.

Preferably the ratio by weight of polymer to polycondensate solids in the composition containing the inorganic binding agent or present in an additive lies in the range from 2:1 to 18:1. The amount of polymer in the composition is preferably in the range of from 1 to 15 percent, especially from 5 to 10 percent by weight based on the weight of the inorganic binding agent.

These ranges may be achieved by adding a polymer dispersion of 50 percent solids content to the building material mixtures in an amount of from 2 to 30% by weight, especially 10 to 20% by weight, calculated on the inorganic binding agent. The polycondensate and polymer dispersion may be incorporated in the form of a pre-mixed composition which may be stabilised with an alkaline agent to the pH ranges mentioned above. The pre-mixed composition may comprise from 25 to 45% polymer and from 2.5 to 12.5% of the polycondensate by weight which may be achieved by mixing the polymer dispersion and the polycondensate solution in a ratio of from 50:50 to 90:10 by weight. In this case, the aqueous polymer dispersion has a solids content of about 50% 100 by weight, the aqueous polycondensate solution of about 25% by weight.

The following examples illustrate the invention.

Example 1.

105 0.20 Part by weight of an alkaline mixture of 80 parts by weight of a 50% aqueous plastics dispersion of vinyl acetate, vinyl chloride and ethylene in a monomer proportion of 60:30:10 and 20 parts by weight of 110 a 25% aqueous solution of a polycondensate of melamine, formaldehyde and sulphite, in a molar proportion of 1:6:3 were added to a test mortar of

- part by weight of Portland cement 115 PZ 350 F
- 1 part by weight of standard sand I
- 2 parts by weight of standard sand II and

The water content of the mortar was ad- 120 justed so that the slump (measure for the plasticity of the mortar) was in the range of from 13 to 18 cm. The water contained in the plastics mixture was allowed for. A strength test according to DIN 1164 was 125 carried out with the mortar by means of prisms of $4 \times 4 \times 16$ cm.

The test data of the compressive strength: are average data of 6 individual measure-

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ments, the data of the tensile strength in bending are average data of 3 individual measurements. In the case of the dry storage, the test specimens were taken from the mould 24 hours after having been prepared, stored in water for 24 hours and then stored at room temperature in a dry state until the strength values were determined. In the case of the wet storage the test specimens were stored in water until the test date, after having removed the mould.

In order to determine the adhesive strength, the test mortar was applied to a ring on a unpretreated concrete base and age hardened at room temperature in the air.

A plate which may be torn off was cemented to the test specimen prior to the test by means of a reactive resin and the adhesive strength was determined by means of the tensile strength apparatus. The test data are average data of 3 individual measurements each time.

The results are shown in the following table 1.

Example 2.

Test mortar was prepared as in example 1, whereby a 50% by weight aqueous plastics dispersion of butyl acrylate and methyl methacrylate in a monomer ratio of 50:50 was used instead of the plastics dispersion of vinyl acetate, vinyl chloride and ethylene.

Example 3.

Test mortar was prepared as in example 1, but with the addition of 0.05 part by 35 weight of an alkaline mixture of 70 parts by weight of a 50% aqueous plastics dispersion of butyl acrylate and methyl methacrylate in a monomer ratio of 50:50 and 30 parts by weight of a 25% aqueous solution of a polycondensate of melamine, formaldehyde and sulphite in a molar ratio of 1:2:1.

Example 4.

Test mortar was prepared as in example 1, but with the addition of 0.10 part by weight 45 of an alkaline mixture of 70 parts by weight of a 50% aqueous plastics dispersion of butyl acrylate and methyl methacrylate in a monomer ratio of 50:50 and 30 parts by weight of a 25% aqueous solution of a polycondensate of melamine, formaldehyde and sulphite, in a molar ratio of 1:2:1.

Example 5.

Test mortar was prepared as in example 1, but with the addition of 0.30 part by weight of an alkaline mixture of 90 parts by weight of a 50% aqueous plastics dispersion of butyl acrylate and methyl methacrylate in a monomer ratio of 50:50 and 10 parts by

weight of a 25% aqueous solution of a polycondensate of melamine, formaldehyde and sulphite in a molar ratio of 1:2:1.

Comparative Examples

The comparative examples were carried out as in example 1, but with the following additives:

Comparative Example C1 was carried out with the addition of 0.08 parts by weight of a 25% aqueous solution of a polycondensate of melamine, formaldehyde and sulphite in a molar ratio of 1:6:3.

Comparative Example C2 was carried out with the addition of 20% by weight calculated on the cement of an aqueous plastics dispersion of methyl methacrvlate and butyl acrylate in a monomer ratio of 50:50 having a 75 solids content of about 50%.

Comparative Example C3 was carried out with the addition of 10% by weight calculated on the cement of a commercial additive of a dispersible powder and a polycondensate according to the instructions of the producer.

The test data indicated in the table are relative values, calculated on the blank mixture (mortar without any plastics addition) for the sake of a better clarity, the tensile strength in bending and the compressive strength of which mixture were fixed at 100.

It can be seen from the comparative examples that a considerable improvement of the adhesive strength results from the addition of the dispersion alone ,on the one hand, but that, on the other hand, a high decrease of the compressive strength takes place, especially in the case of the wet storage.

An addition of the sulfonated melamine/ formaldehyde condensate alone (comparative example 1) leads to a well-balanced relation of the tensile strength in bending and the compressive strength.

The adhesive strength is scarcely affected, 100 however.

The use of the dispersible powder (comparative example 3) results in a favourable tensile strength in bending and compressive strength proportion in the case of a dry stor- 105 age, but considerably reduces both values in the case of a wet storage. The adhesive strength is scarcely improved.

By using the aqueous plastics dispersion according to the invention together with an 110 aqueous solution of the sulfonated melamine formaldehyde condensate, the latter solution being possibly contained in the freshly mixed mortar, a balanced ratio of tensile strength in bending and compressive strength, as well 115 as an improved adhesive strength is obtained, which may even reach the characteristic tensile strength of the mortar.

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TABLE

				Dry S	Dry Storage			Wet S	Wet Storage		
		11,04	Bending	Bending Strength	Compress	Compressive Strength	Bending	Bending Strength	Compressi	Compressive Strength	Adhesion
Example	Slump (cm)	water- cement factor	after 7 days	after 28 days	after 7 days	after 28 days	after 7 days	after 28 days	after 7 days	after 28 days	after 28 days
Blank	14.6/14.5	0.50	100	100	100	100	100	100	100	100	1-2
	14,4/14.6	0.41	128	114	92	92	104	91	91	82	10.0
2	17.5 18.0	0.40	151	159	104	116	110	102	93	100	23.5
æ	15,4/15.6	0.48	115	110	92	94	100	86	06	104	8.7
4	14.5/14.6	0.46	129	123	103	107	101	100	92	67	19.0
٠	15.8/15.9	0.42	150	140	105	120	103	106	88	86	25.0
C.1	15.5/15.8	0.46	115	111	106	106	113	92	104	86	2.0
C.2	14.3,/14.5	0.42	139	122	83	80	66	100	100	78	22.1
C,3	14.0,14.5	0,44	111	107	87	76	06	80	83	76	4.6
	5 10 15	WHAT WE CLAIM IS:— 1. A composition comprising an inorganic binding agent, a sulphite modified polycondensate of formaldehyde and an amino - s triazine, and a polymer of one or more olefinically unsaturated monomers, the said polymer having been incorporated in the form of an aqueous dispersion formed by an emulsion polymerization process. 2. A composition as claimed in claim 1, wherein the inorganic binding agent comprises cement. 3. A composition as claimed in claim 1 or claim 2, wherein the composition comprises the ingredients of concrete or mortar. 4. A composition as claimed in any one of	T WE CLAIM IS:— composition comprisis agent, a sulphite mo of formaldehyde and and a polymer of one nsaturated monomers, ving been incorporate lucous dispersion form ymerization process. composition as claim the inorganic binding to a composition as claim a 2, wherein the con the ingredients of concine ingredients of co	WHAT WE CLAIM IS:— 1. A composition comprising an inorganic nding agent, a sulphite modified polyconsiste, and a polymer of one or more olefinazine, and a polymer of one or more olefinally unsaturated monomers, the said polyer having been incorporated in the form an aqueous dispersion formed by an emulon polymerization process. 2. A composition as claimed in claim 1, herein the inorganic binding agent comprises ment. 3. A composition as claimed in claim 1 claim 2, wherein the composition comises the ingredients of concrete or mortar. 4. A composition as claimed in any one of	inorganic polyconino - s - re olefinaid poly-the form an emulcial 1, comprises claim 1 on commontar.	claims 1 to 3, wherein the amino - s - triazine has at least two amino groups. 5. A composition as claimed in any one of claims 1 to 3, wherein the amino - s - triazine is melamine. 6. A composition as claimed in any one of claims 1 to 5, wherein an alkali has been incorporated into the composition. 7. A composition as claimed in any one of claims 1 to 6, wherein the polymer comprises units of a vinyl ester, an acrylic acid ester, a methacrylic acid ester, a methacrylic acid ester, a vinyl halide, a vinylidene halide, an unsaturated hydrocarbon, or acrylonitrile, or a mixture of two or more of these units. 8. A composition as claimed in any one	to 3, wherein the ast two amino gr composition as classification as composition as classification as the composition as classification as classification as classification as classification as classification as carylonitrile, or of these units.	aims 1 to 3, wherein the amino - s - triazine is at least two amino groups. 5. A composition as claimed in any one claims 1 to 3, wherein the amino - s - trinine is melamine. 6. A composition as claimed in any one claims 1 to 5, wherein an alkali has been corporated into the composition. 7. A composition as claimed in any one of aims 1 to 6, wherein the polymer comprises lits of a vinyl ester, an acrylic acid ester, methacrylic acid ester, a vinyl halide, a nylidene halide, an unsaturated hydrocarnh, or acrylonitrile, or a mixture of two more of these units. 8. A composition as claimed in any one	s - triazine in any one in - s - tri- in any one li has been l. any one of r comprises acid ester, l halide, a hydrocar- ire of two in any one	30 25	

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of claims 1 to 7, wherein the polymer comprises units of vinyl acetate, vinyl propionate, vinyl isobutyrate, vinyl laurate, vinyl esters of tertiary acids having from 9 to 11 carbon 5 atoms, ethyl acrylate, methyl methacrylate, vinyl chloride, vinylidene chloride, ethylene, styrene, vinyl toluene, or butadiene, or a mixture of two or more of these units.

9. A composition as claimed in any one of claims 1 to 8, wherein the polymer is a substantially alkali resistant polymer.

- 10. A composition as claimed in any one of claims 1 to 9, wherein the polymer is a vinyl acetate/vinyl chloride, vinyl propion15 ate/vinyl chloride, vinyl acetate/ethylene, vinyl acetate/vinyl chloride/ethylene, vinyl acetate/vinyl chloride/vinyl laurate, styrene/butyl acrylate, styrene/butyl acrylate, styrene/butyl acrylate, butyl acrylate/methyl meth20 acrylate, or butyl acrylate/vinylidene chloride copolymer or a copolymer of vinyl acetate and vinyl esters of tertiary acids having from 9 to 11 carbon atoms.
- 11. A composition as claimed in any one of claims 1 to 10, wherein the polymer is substantially a 60:30:10:vinyl acetate/vinyl chloride/ethylene copolymer or substantially a 50:50 butyl acrylate/methyl methacrylate copolymer.

12. A composition as claimed in any one of claims 1 to 11, wherein the amount of polymer in the composition is in the range of from 1 to 15 per cent by weight based on the weight of the inorganic binding agent.

13. A composition as claimed in claim 12, wherein the amount of polymer in the composition is in the range of from 5 to 10 per cent by weight based on the weight of the inorganic binding agent.

14. A composition as claimed in any one of claims 1 to 13, wherein the ratio of polymer to polycondensate is in the range of from 2:1 to 18:1 by weight.

15. A process for the preparation of a

composition as claimed in any one of claims 1 to 14, which comprises admixing the inorganic binding agent, the sulphurous acid or sulphite modified polycondensate of formaldehyde and amino - s - triazine and the polymer, the polymer being incorporated in the form of an aqueous dispersion formed by an emulsion polymerization process.

16. A process as claimed in claim 16, wherein the polycondensate is admixed in aqueous solution.

17. A process as claimed in claim 16, wherein the aqueous solution comprises substantially 25 percent by weight of the polycondensate.

18. A process as claimed in any one of claims 15 to 17, wherein a pre-mixed composition comprising the sulphurous acid or sulphite modified polycondensate of formaldehyde and amino - s - triazine in aqueous solution, and the said polymer in the form of an aqueous dispersion formed by an emulsion polymerization process is incorporated.

19. A process for making mortar and concrete which comprises admixing a polymeric material consisting of polymerized units of olefinically unsaturated monomers and a polycondensate of formaldehyde and an amino s - triazine modified with sulphite or sulphurous acid, with fresh mortar or concrete, wherein the polymeric material is incorporated in the form of an aqueous dispersion formed by an emulsion polymerization process.

20. A composition as claimed in claim 1, substantially as described in any one of the 8 Examples herein.

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